PATENT SPECIFICATION

(11) 1 420 839

1 420 839

(21) Application No. 24842/73 (22) Filed 24 May 1973
(31) Convention Application No. 257 524 (32) Filed 30 May 1972 in
(33) United States of America (US)
(44) Complete Specification published 14 Jan. 1976
(51) INT CL² C08K 5/19 // G03G 9/02
(52) Index at acceptance
C3P 7D2A1 E2 PC16A PC17 PC18 PC8A PC8B PC8C
C3R 3C 3N7 C10 C11 C12 C13P C14A C14B C1 C5A C6A1 L2C1 L5A
G2H 5D1A 5D1Y 5DY 5G1A 5G1Y 5G2A 5G2G1 5G2G4 5G2GX 5G2X 5G2Y 5G4D 5G4Y 5GY 5Y

(19)

(72) Inventors BRUCE JOEL RUBIN, ALEC NAFTALI MUTZ and THOMAS ARTHUR JADWIN

(54) TONER COMPOSITIONS

(71) We, EASTMAN KODAK COMPANY, a Company organized under the Laws of the State of New Jersey, United States of America, of 343 State Street, Rochester, New York 14650, United States of America do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to particulate toner compositions useful in the development of electrostatic charge images.

Electrographic imaging and developing processes, e.g. electrophotographic imaging processes and techniques have been extensively described in both the patent and other literature. Generally these processes have in common the steps of forming a latent electrostatic charge image on an insulating electrographic material. The electrostatic latent image is then rendered visible by a development step in which the charged surface of the electrographic material is brought into contact with a suitable developer mix. Conventional dry developer mixes include toner sometimes called "marking particles" and can also include a carrier vehicle that can be either a magnetic material such as iron filings, powdered iron or iron oxide, or a triboelectrically chargeable, nonmagnetic substance like glass beads or crystals of inorganic salts such as sodium or potassium fluoride. The toner typically contains a resinous material suitably coloured or darkened, for contast purposes, with a colorant like dyestuffs or pigments such as carbon black.

One method for applying a suitable dry developer mix to a charged image-bearing electrographic element is by the well-known magnetic brush process. Such a process generally utilizes an apparatus of the type described, for example, in U.S. Patent No. 3,003,462 and customarily comprises a nonmagnetic rotatably mounted cylinder having fixed magnetic means mounted inside. The cylinder is arranged to rotate so that part of the surface is immersed in, or otherwise contacted with, a supply of developer mix. The granular mass comprising the developer mix is magnetically attracted to the surface of the cylinder. As the developer mix comes within the influence of the field generated by the magnetic means within the cylinder, particles thereof arrange themselves in bristle-like formations resembling a brush. The brush formations that are formed by the developer mix tend to conform to the lines of magnetic flux, standing erect in the vicinity of the poles lying substantially flat when said mix is outside the environment of the magnetic poles. Within one revolution the continually rotating cylinder picks up developer mix from a supply source and returns part or all of this material to this supply. This mode of operation assures that fresh mix is always available to the surface of the charged electrographic element at its point of contact with the brush. In a typical rotational cycle, the roller performs the successive steps of developer mix pickup, brush formation, brush contact with the electrographic element (e.g. a photoconductive element), brush collapse and finally mix release.

In magnetic brush development, as well as in various other types of electrographic development wherein a dry triboelectric mixture of a particulate carrier vehicle and a toner powder are utilized (e.g., cascade development such as described in US Patents 2,638,416 and 2,618,552), it is advantageous to modify the surface properties of the toner powder so that a net electrical charge that is uniform, stable and high can be imparted to the toner powder by the particulate carrier vehicle.

In accordance with the present invention, it has been discovered that certain salts incorporated in a dry, particulate toner composition comprising a resin and, if desired, a suitable

colorant such as a pigment or dye, provide an effective charge control agent for the toner composition.

According to the present invention there is provided a dry particulate toner composition having particles comprising a resin having incorporated therein a quaternary ammonium charge control agent having the formula:—

$$\begin{array}{c} R^2 \\ | \\ R^1\!-\!N^+\!-\!R^3 \\ | \\ R^4 \end{array} \qquad X^-$$

wherein R^1, R^2, R^3 and R^4 may be the same or different and represent an aliphatic hydrocarbon group containing up to seven carbon atoms and X^- represents an anionic function.

Toner materials of the invention containing the described quaternary ammonium salt charge control agents have been found effective in providing particulate toner compositions which exhibit net toner charges that are relatively high, uniform and stable when admixed with a suitable particulate carrier vehicle. The present toner materials also exhibit a minimal amount of deleterious toner throwoff when used to develop electrostatic charge images.

In addition, the quaternary ammonium charge control agents used in the present invention have been found to have little or no deleterious effect on the adhesion to conventional paper receiving sheets of the resultant toner composition containing these charge control agents.

Moreover, it has been found that resinous toner particles containing an effective amount of the above-described quaternary ammonium charge control agents generally result in good to excellent electrographic images exhibiting increased and uniform density with little or no background scumming.

The resins useful in the practice of the present invention can be used alone or in combination and include those resins conventionally employed in electrostatic toners. Useful resins generally have a glass transition temperature within the range of from 60° to 120°C. Preferably, toner particles prepared from these resinous materials have relatively high caking temperature, for example, higher than 55°C., so that the toner powders may be stored for relatively long periods of time at fairly high temperatures without having individual particles agglomerate and clump together. The melting point of useful resins preferably is within the range of from 65°C. to 200°C. so that the toner particles can readily be fused to conventional paper receiving sheet to form a permanent image. Especially preferred resins are those having a melting point within the range of from 65°C. to 120°C. Of course, where other types of receiving elements are used, for example, metal plates such as certain printing plates, resins having a melting point and glass transition temperature higher than the values specified above may be used.

As used herein the terms "melting point" refers to the melting point of a resin as measured by Fisher Johns apparatus, Fisher Scientific Catalog No. 12—144. Glass transition temperature (Tg) as used herein refers to the temperature at which a polymeric material changes from a glassy polymer to a rubbery polymer. This temperature (Tg) can be measured by differential thermal analysis as disclosed in *Techniques and Methods of Polymer Evaluation*, Vol. 1, Marcel Dekker, Inc., N.Y. 1966.

Among the various resins which can be employed in the toner particles of the present invention are polystyrene containing resins, polycarbonates, polyamides, phenol-formaldehyde resins and various derivatives thereof, polyester condensates, modified alkyd resins including rosin modified maleic alkyl resins and aromatic resins containiing alternating methylene and aromatic units.

Typical useful toner resins include certain polycarbonates such as those described in French Patent 2,090,986, and which patent discloses polycarbonate materials containing an alkylidene diarylene group in a recurring unit and having from 1 to 10 carbon atoms in the alkylidene portion. Other useful resins having the above-described physical properties include polymeric esters of acrylic and methacrylic acid such as poly(alkylacrylate) and poly-(alkylmethacrylate) wherein the alkyl portion can contain up to 10 carbon atoms. Additionally, other polyesters having the aforementioned physical properties are also useful. Among such other useful polyesters are copolyesters prepared from terephthalic acid including substituted terephthalic acid, a bis-(hydroxyalkoxy phenyl)alkane having up to 4 carbon atoms in the alkoxy radical and up to 10 carbon atoms in the alkane radical and including halogen substituted alkanes, and an alkylene glycol having up to 4 carbon atoms in the alkylene portion.

Other useful resins are various styrene-containing resins. Such polymers typically comprise a polymerized blend of from 40 to 100 percent by weight of styrene, from 0 to 45 percent by weight of a lower alkyl acrylate or methacrylate having up to 4 carbon atoms in the alkyl portion such as methyl, ethyl, isopropyl or butyl, and from 5 to 50 percent by weight of another vinyl monomer other than styrene, for example, a higher alkyl acrylate or methacrylate having from 6 to 20 or more carbon atoms in the alkyl group. A typical styrene-containing resin prepared from a copolymerized blend as described hereinabove are copolymers prepared from a monomeric blend of 40 to 60 percent by weight styrene or styrene homolog, from 20 to 50 percent by weight of a lower alkyl acrylate or meth-

acrylate and from 5 to 30 percent by weight of a higher alkyl acrylate or methacrylate such as 2-ethylhexyl acrylate. A variety of other useful styrene containing toner materials are disclosed in the following U.S. Patents: 2,917,460, Re. 25,136, 2,788,288, 2,638,416, 2,618,552 and 2,659,670.

The toner particles of the present invention can be prepared by various methods. One convenient technique for preparing these toners is spray-drying. Spray-drying involves first dissolving the polymer, the toner colorant and the charge control agent in a volatile organic solvent such as dichloromethane. This solution is then sprayed through an atomizing nozzle using a substantially nonreactive gas such as nitrogen as the atomizing agent. During atomization, the volatile solvent evaporates from the airborne droplets, producing toner particles of the uniformly dyed or pigmented resin. The ultimate particle size is determined by varying the size of the atomizing nozzle and the pressure of the gaseous atomizing agent. Particles of a diameter between 0.1 micron and 100 microns may be used, although in general present day office copy devices typically employ particles between 1.0 and 30 microns. However, larger particles of smaller particles can be used where desired for particular methods of development or particular development conditions. For example, in powder cloud development such as described in U.S. Patent 2,691,345, extremely small toner particles are used.

Another convenient method for preparing the toner composition of the present invention is melt-blending. This technique involves melting a powdered form of polymer or resin and mixing it with suitable colorants, such as dyes or pigments, and the charge control agent. The resin can readily be melted on heated compounding rolls which are also useful to stir or otherwise blend the resin and addenda so as to promote the complete intermixing of these various ingredients. After thorough blending, the mixture is cooled and solidified. The resultant solid mass is then broken into small particles and finely ground to form a free-flowing powder of toner particles. These particles typically have an average particle size or average diameter within the range of from 0.1 to 100 microns.

As described hereinabove the quaternary ammonium charge control agents used in the invention are added to the resinous toner composition in an amount effective to improve the charge properties of the toner composition. The addition of a charge control agent improves the charge uniformity of a particular toner composition, i.e. acts to provide a toner composition in which all or substantially all of the individual discrete toner particles exhibit a triboelectric charge of the same sign (negative or positive) with respect to a given carrier vehicle, increases the net electrical charge exhibited by a specified quantity of toner particles relative to a given carrier vehicle, and reduces the amount of "toner throw-off" of a given toner composition. As used herein, the phrases "net electrical charge exhibited by a toner powder" or "net toner charge" are equivalent and are defined as the total electrical charge exhibited by a specified amount of a particular toner when admixed with a specified amount of a particular carrier vehicle. Although the phenomenon by which such an electrical charge is imparted is not fully understood, it is believed due in large to the triboelectric effect caused by the physical admixture of toner and carrier. As used herein, the term "toner throw-off" is defined as the amount of toner powder thrown out of a developer mix as it is mechanically agitated, e.g., in a development apparatus. Aside from the extraneous contamination problems inherent with airborne toner dust in the development apparatus, "toner throw-off" also leads to imaging problems such as unwanted background and scumming of the electrographic image-bearing material.

Generally, it has been found desirable to add from 0.1 to 6 parts and preferably 0.3 to 3.0 parts by weight of the aforementioned quaternary ammonium salts per 100 parts by weight of a resinous binder to obtain the improved toner composition of the present invention. Although larger and smaller amounts of a charge control agent can be added, it has been found that if amounts much lower than those specified above are utilized, the charge control agent tends to exhibit little or substantially no improvement in the properties of the toner composition. As amounts more than about 6 parts of charge control agent per 100 parts of resinous binder are added, it has been found that the net toner charge exhibited by the resultant toner composition tends to be reduced. The optimum amount of charge control agent to be added will depend, in part, on the particular quaternary ammonium charge control agents selected and the particular resinous binder to which it is added. However, the amounts specified hereinabove are typical of the useful range of charge control agent utilized in conventional dry toner materials.

As indicated, the quaternary ammonium charge control agents contemplated for use according to the present invention have the formula:

$$\begin{array}{ccccc} & & R^2 & & \\ & & | & & \\ R^1 & — & N^+ & — & R^3 \\ & & | & & \\ & & R^4 & & \end{array} \qquad X^-$$

wherein each of R^1, R^2, R^3 and R^4 may be the same or different and represent an aliphatic hydrocarbon moiety having up to 7 carbon

atoms, and X^- is an anionic function. Each of R^1, R^2, R^3 and R^4 can be a straight-chain or branched-chain aliphatic hydrocarbon group including allyl and alkyl groups, e.g. methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl and isopropyl. Especially good results have been obtained wherein R^1, R^2, R^3 and R^4 each represent a group having from 3 to 7 carbon atoms and more particularly wherein each of R^1, R^2, R^3 and R^4 represents an identical alkyl group having from 3 to 7 carbon atoms. As can be observed from the above list, a variety of hydrocarbon substituents may be utilized in the quaternary ammonium salt charge control agents of the present invention. In addition, a variety of conventional anionic groups can be utilized such as the following: halides; phosphates; acetates; nitrates; benzoates, methyl sulphate; perchlorate; tetrafluoro-borate or benzenesulphonate. Especially useful anionic groups are the halides. Typical of the quaternary salts useful in the invention are the following:

Tetrapentylammonium chloride
Tetraheptylammonium chloride
Tetrapentylammonium hexafluorophosphate
Tetraethylammonium benzoate
Tetraethylammonium acetate tetrahydrate
Tetrapentylammonium bromide
Tetrabutylammonium iodide
Tetrabutylammonium nitrate
Triethylmethylammonium iodide

A variety of colorant materials selected from dyestuffs or pigments may be employed in the toner materials of the present invention. Such materials serve to colour the toner and/or render it more visible. Of course, suitable toner materials having the appropriate charging characteristics can be prepared without the use of a colorant material where it is desired to have a developed image of low optical opacity. In those instances where it is desired to utilize a colorant, the colorants used, can, in principle, be selected from virtually any of the compounds mentioned in the *Colour Index* Volumes 1 and 2, Second Edition.

Included among the vast number of useful colorants would be such materials as Hansa Yellow G (C.I. 11680), Nigrosine Spirit soluble (C.I. 50415), Chromogen Black ET00 (C.I. 45170), Solvent Black 3 (C.I. 26150), Fuchsine N (C.I. 42510) and C.I. Basic Blue 9 (C.I. 52015). Carbon black also provides a useful colorant. The amount of colorant added can vary over a wide range, for example, from 1 to 20 percent of the weight of the thermoplastic resin. Particularly good results are obtained when the amount is from 2 to 10 percent. In certain instances, it is be desirable to omit the colorant, in which case the lower limit of concentration would be zero.

The toners of this invention can be mixed with a carrier vehicle to form developing compositions. The carrier vehicles which can be used with the present toners to form new developer compositions can be selected from a variety of materials. Suitable carrier vehicles useful in the invention include various non-magnetic particles such as glass beads, crystals of inorganic salts such as sodium or potassium chloride, hard resin particles, or metal particles. In addition, magnetic carrier particles can be used in accordance with the invention. In fact, the toner compositions of the present invention are especially suited for use with magnetic carrier particles as the problem of "toner throw-off" is especially bothersome in magnetic brush development processes. Suitable magnetic carrier particles are particles of ferromagnetic materials such as iron, cobalt, nickel, and alloys and mixtures thereof. Other useful magnetic carriers are ferromagnetic particles overcoated with a thin layer of various film-forming resins, for example, the alkali-soluble carboxylated polymers described in U.S. Patents 3,547,822, 3,632,512. Other useful resin coated magnetic carrier particles include carrier particles coated with various fluorocarbons such as polytetrafluoroethylene, polyvinylidene fluoride, and mixtures thereof including copolymers of vinylidene fluoride and tetrafluoroethylene.

A typical developer composition containing the above-described toner and a carrier vehicle generally comprises from 1 to 10 percent by weight of particulate toner particles and from 90 to 99 percent by weight carrier particles. Typically, the carrier particles are larger than the toner particles. Conventional carrier particles have a particle size on the order of from 30 to 1200 microns, preferably 60—300 microns.

The toner and developer compositions of this invention can be used in a variety of ways to develop electrostatic charge patterns or latent images. Such developable charge patterns can be prepared by a number of means and be carried, for example, on a light sensitive photoconductive element or a non-light sensitive dielectric-surfaced element such as a receiver sheet. One suitable development technique involves cascading the developer composition across the electrostatic charge pattern; while another technique involves applying toner particles from a magnetic brush. This latter technique involves the use of a magnetically attractable carrier vehicle in forming the developer composition. After imagewise deposition of the toner particles, the image can be fixed by heating the toner to cause it to fuse to the substrate carrying the toner. If desired, the unfused image can be transferred to another support such as a blank sheet of copy paper and then fused to form a permanent image.

The following examples are included for a further understanding of the invention.

Example 1.

A poly(4,4'-isopropylidene diphenylene-alt-ethylene carbonate) resin as described in French Patent 2,090,986 was melted on a rubber compounding mill at a temperature of between 125°—150°C. Cabot Corporation 'Sterling' FT Carbon Black was added to yield 5.7 parts of carbon black per 100 parts of polymer. 'Sterling' is a registered Trade Mark. This carbon black-polycarbonate composition was then used as a control toner. A variety of different materials were then added to individual samples of the control toner as described below and then the net toner charge and toner throw-off were measured for each of the sample toner compositions to test the charge control capabilities of the various materials added to the toner.

Each toner sample was prepared by blending all ingredients together on the rubber compounding mill for approximately 20 minutes. Each melt was then cooled to room temperature and ground in a laboratory disk grinder to pass through a 20 mesh screen (A.S.T.M.) Final grinding to a particle size less than 30 microns was accomplished in a fluid energy mill. The net toner charge was measured by mixing 6 percent of the toner with an insulating polymer-coated particulate carrier comprising an oxidized sponge iron core, e.g. rough surfaced iron particles 80 to 120 mesh obtained from Hoeganaes Corporation coated with a polymer of 15 mole percent acrylonitrile, 79 mole percent vinylidene chloride and 6 mole percent acrylic acid. The mixing was accomplished by placing the carrier and toner in a small paper cup which was then rolled on a roll mill for 15 minutes. The net toner charge was measured using a Faraday Cage in the following manner: a weighed portion of each of the developers was placed in an iron tube that was covered at one end with a 200 mesh screen that retains all carrier particles within the tube. The iron tube was connected in series with a capacitor to the ground. An air stream was then directed through the tube, blowing toner particles off the carrier, through the 200 mesh screen at the exit end. The potential resulting on the capacitor was measured by an electrometer. The potential obtained was converted to electrical charge in microcoulombs and this figure was divided by the weight in grams of the toner that was removed from the tube, providing the net toner charge in microcoulombs per gram.

In addition to net toner charge, a test was devised to measure the toner throw-off exhibited by each of the sample toners when admixed with a particulate carrier vehicle as follows: A fixed quantity of a well-mixed developer (i.e. mixture of toner and carrier particles) was measured and placed in an open cup positioned in a device oscillating laterally through a 0.75 inch distance at 6 cycles per second for a fixed period of time. The toner throw-off of the developer mix due to the oscillation was collected on filter paper via a vacuum and weighed. The amounts so weighed are reported in Table I below in milligrams.

TABLE I

Charge Agent	Concentration (parts/100 parts polycarbonate)	Charge (μ coul/g)	Throw-off (mg)
Control (no charge agent)	—	0.4	350.7
Tetrapentylammonium chloride (TPACL)	0.1	10.6	18.3
TPACL	0.3	12.4	14.4
TPACL	0.5	14.3	3.6
TPACL	1.0	13.0	4.2
TPACL	1.5	13.3	1.6
TPACL	3.0	12.5	5.2
TPACL	6.0	7.6	46.4 (Avg)
Tetraheptylammonium chloride (THACL)	0.3	10.1	Not available (N.A.)
THACL	0.5	14.6	N.A.
THACL	1.0	11.6	N.A.
Tetrapentylammonium hexafluorophosphate (TPAFP)	0.5	8.9	N.A.
TPAFP	1.0	9.8	N.A.
TPAFP	2.0	7.9	N.A.
Tetraethylammonium benzoate (TEAB)	1.0	11.4	4.0
TEAB	3.0	5.0	45.3
Tetraethylammonium acetate tetrahydrate (TEAAT)	0.5	7.7	2.6
TEAAT	1.0	11.4	3.4
Tetrapentylammonium bromide (TPAB)	0.25	12.2	N.A.
TPAB	0.5	15.7	N.A.
TPAB	1.0	12.3	3.7
TPAB	3.0	10.1	N.A.
Tetrabutylammonium iodide (TBAI)	0.5	13.5	8.6
TBAI	1.0	10.8	4.1
TBAI	1.5	11.5	4.9
TBAI	3.0	9.9	11.2
Tetrabutylammonium nitrate (TBAN)	1.0	11.7	4.9
TBAN	3.0	10.2	6.3

Example 2.

Toners were prepared and tested according to Example 1, except that a polystyrene resin (Piccolastic D125) was substituted for the polycarbonate and 6.0 parts of the carbon black were used per 100 parts of polymer. The results obtained are given in Table II.

TABLE II

Charge Agent	Concentration (parts/100 parts Piccolastic D125)	Charge (μ coul/g)	Throw-off (mg)
Control (no charge agent)	—	2.6	188.5
Tetrapentylammonium chloride (TPAC)	0.1	6.6	20.7
TPAC	0.5	8.0	16.5

These results indicate that the significant effect on charge obtained with the charge control agents used in the present invention is applicable to a variety of polymeric binders and is not restricted to the use of polycarbonate binders.

Electrophotographic electrostatic charge patterns obtained in the conventional manner and processed with developer compositions containing the charge control agents used in the present invention provide images that are dense and sharp with little or no colouration, i.e. depositions of toner particles, in non-image background areas, toner "throw-off" of dusting in magnetic brush processes is minimal and the prints containing the transferred images can be handled repeatedly, bent, folded and the like without causing undue "flake-off" of the image thereon (See Example 3).

Example 3.

A toner with one part tetrabutylammonium nitrate and 5.7 parts Sterling FT carbon black per 100 parts resin was prepared according to Example 1. The toner was mixed with a magnetic carrier as described in Example 1 at 6% concentration. This resultant developer was placed in a magnetic brush of the general type described in U.S. Patent 3,003,462. An organic photoconductor-containing element bearing a latent electrostatic charge image was passed over the magnetic brush. The toned image thus formed on the photoconductor-containing element was subsequently transferred to paper. The toned image was fused to paper with an infrared lamp. Using the above-described developer, the magnetic brush exhibited low toner throw-off. The images that were formed were sharp, of high density, and

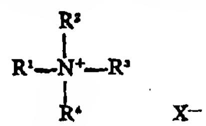
advantageously exhibit very low background coloration. The images, after fusing, exhibited good adhesion to paper.

Example 4.

A toner with 0.5 parts tetrapentylammonium chloride and 5.7 parts 'Sterling' FT carbon black per 100 parts resin were prepared according to Example 1. The toner was mixed with a carrier described in Example 1 at 6% concentration. This resultant developer was placed in a magnetic brush of the general type described in U.S. Patent 3,003,462. An organic photoconductor-containing element bearing a latent electrostatic charge image was passed over the magnetic brush. The toned image thus formed on the photoconductor-containing element was subsequently transferred to paper. The toned image was fused to paper with an infrared lamp. Using the above-described developer, the magnetic brush exhibited low toner throw-off. The images that were formed were sharp, of high density, and advantageously exhibited very low background coloration. The images, after fusing, exhibited good adhesion to paper.

WHAT WE CLAIM IS:—

1. A dry particulate toner composition having particles comprising a resin having incorporated therein a quaternary ammonium charge control agent having the formula:



wherein R^1, R^2, R^3 and R^4 may be the same or different and represent an aliphatic hydrocarbon group containing up to seven carbon atoms and X^- represents an anionic function.

2. A composition as claimed in Claim 1, in which the charge control agent is present in a concentration from 0.1 to 6 parts by weight per 100 parts by weight of the resin.

3. A composition as claimed in Claim 2, in which the charge control agent is present in a concentration from 0.3 to 3 parts by weight per 100 parts by weight of the resin.

4. A composition as claimed in Claim 4, in which R^1, R^2, R^3 and R^4 each represent an alkyl group containing from 3 to 7 carbon atoms.

5. A composition as claimed in any preceding Claim, in which X^- represents a halide anion, a phosphate anion, an acetate anion or a nitrate anion.

6. A composition as claimed in Claim 5, in which X^- represents a halide anion.

7. A composition as claimed in Claim 6, in which X^- represents a chloride anion.

8. A composition as claimed in any preceding Claim, in which the particles have a size in the range from 0.1 micron to 100 microns.

9. A composition as claimed in Claim 8, in which the particles have a size in the range from 1 to 30 microns.

10. A composition as claimed in any preceding Claim, in which the resin has a melting point in the range from 65 to 200°C.

11. A composition as claimed in Claim 10, in which the resin has a melting point in the range from 65 to 120°C.

12. A composition as claimed in any preceding Claim, in which the resin has a glass transition temperature in the range from 60 to 120°C.

13. A composition as claimed in any preceding Claim, which comprises a styrene containing resin.

14. A composition as claimed in Claim 13, in which the resin contains from 40 to 100 percent by weight styrene (or styrene homologue) units, from 0 to 45 percent by weight of alkyl acrylate or methacrylate units having from 1 to 4 carbon atoms in the alkyl group and from 5 to 50 percent by weight of alkyl acrylate or methacrylate having from 6 to 20 carbon atoms in the alkyl group.

15. A composition as claimed in any of Claims 1 to 12, which comprises a polycarbonate-containing resin.

16. A composition as claimed in any preceding Claim, in which the particles further comprise a pigment or dyestuff in an amount sufficient to colour the composition.

17. A composition as claimed in Claim 16, which the particles contain carbon black as pigment.

18. A toner composition as claimed in Claim 1, substantially as described in any of the Examples herein.

19. An electrographic developer composition comprising carrier particles and a toner composition as claimed in any of the preceding Claims.

20. A developer composition as claimed in Claim 19 in which the carrier particles are ferromagnetic.

21. A developer composition as claimed in Claim 19, substantially as described in any of the Examples herein.

L. A. TRANGMAR,
B.Sc., C.P.A.,
Agent for the Applicants.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1976.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.